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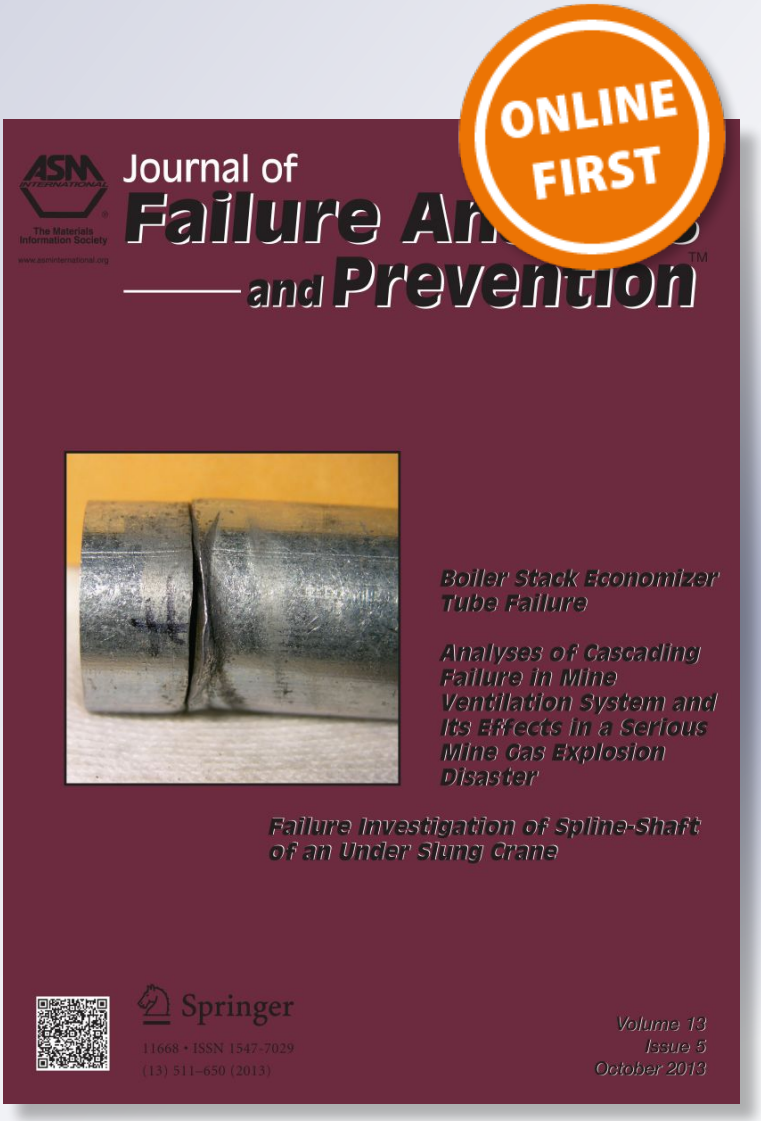

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TECHNICAL ARTICLE—PEER-REVIEWED

Unexpected High-Energy Failure of Type 304L Stainless Steel Piping in the Tail Gas System in Nitric Acid Plant Due to Intergranular Stress Corrosion Cracking (IGSCC)

Daniel J. Benac · Nicholas Cherolis · Mike Hester

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Abstract An incident occurred at a Nitric Acid Plant when a failed 18-in. (457 mm)-diameter 304L stainless steel pipe connecting the Converter to the Tail Gas Catalytic Reactor ruptured. The rupture resulted in thrown fragments and some damage to equipment in the vicinity of the pipe. Normally, pipe operating conditions are about 80 psig (0.55 MPa) and 850–900 °F (454–482 °C), and the nominal thickness of the pipe was 0.180-in. (0.46 mm). This article summarizes the discovery of a very unusual condition of intergranular stress corrosion cracking due to sensitization of the low-carbon stainless steel used in manufacture of the pipe. The lessons learned from this failure investigation are vital to those who use stainless steel in Tail Gas systems.

Keywords Rupture · Type 304L · Sensitization · IGSCC · Nitric acid · Explosion

Introduction

At a Nitric Acid Plant, an 18-in. (457 mm)-diameter Type 304L stainless steel pipe from the Converter (201-D) to the Tail Gas Catalytic Reactor (202-D) suddenly ruptured, resulting in ejection of pipe fragments through the roof and damage to equipment in the vicinity of the pipe. The ruptured line had been in service for approximately 18 years. An investigation was ordered, to determine the failure mechanism of the pipe.

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Background

Material of Construction

The Nitric Acid Plant pipe was an 18-in. (457 mm)-diameter 304L stainless steel pipe connecting the Converter (201-D) to the Tail Gas Catalytic Reactor (202-D). The nominal wall thickness of the pipe was 0.180-in. (0.46 mm). The tail gas pipe assembly included a designed "kink" or "jog" in the pipe configuration, requiring a miter section to be fabricated to join the horizontal and the vertical pipe. The pipe was cold-worked, formed, and welded plate consisting of a two-part welded construction. According to the drawing, the pipe was originally designed in 1996. The pipe had not been replaced or repaired after the original installation (Fig. 1).

Operating Conditions

Prior to the incident, the plant was operating normally. The typical pipe operating conditions were a pressure of 80 psig (0.55 MPa) and temperature of 850–900 °F (454–482 °C). The design condition was a pressure of 100 psig (0.69 MPa) and temperature of 1100 °F (593 °C). The actual pressure at the time of the incident was 75 psig (0.52 MPa), and the temperature was 810 °F (432 °C).

Investigation

On-Site Observations

On-site investigation was performed on the 18-in. (457 mm)-diameter 304L stainless steel pipe that connected the Acid Plant Converter to the Tail Gas Catalytic

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Reactor, (see Fig. 2). The event failed the upper part of the pipe wall in the miter section, producing two large "flaps" that remained attached to the pipe, and some smaller fragments that were thrown (Fig. 3). There was evidence of brown staining on the pipe and in the immediate vicinity that was likely due to the release of NO_x after the failure. NO_x is a generic term for the mono-nitrogen oxides NO and NO_2 (nitric oxide and nitrogen dioxide), which are produced from the reaction among nitrogen, oxygen, and even hydrocarbons (during combustion), especially at high temperatures. Several of the pipe fragments penetrated the building room, as shown in Fig. 4; those fragments were not recovered. Additional minor damage included a broken window (Fig. 5), upward throw of the grating above the failure location, and damage to a firewater pipe above the failure. It was noted that the window that was broken was of light construction; therefore, it was not conclusive as to whether the damage was caused by pressure from the event or due to a fragment impact.

The metal "flaps" were examined in place and found to have extensive cracking on their inside surfaces and thick-walled edges, as shown in Figs. 6 and 7. The inside of the pipe looking upstream appeared clean, without any deposits or foreign material.

The "flaps" were marked and removed from the pipe for examination, and the pipe itself was removed. A stamped marking was found on the outer wall of Piece 2 (larger flap), as shown in Fig. 8, which appeared to show markings of "304L," "81105," and likely "R0975." The horizontal pipe shifted by several inches when pieces of it were cut out for the investigation, an indication that the pipe had been under residual stress while in place.

Fragment Throw Analysis

There was a concern that an internal explosion may have occurred to cause the rupture. A pipe burst calculation [1] was performed to determine whether a failure at the nominal working pressure of 80 psig (0.55 MPa) could throw fragments through the roof of the building, creating the holes observed. This calculation assumed a pipe wall thickness of 0.18 in. (0.46 mm) and nitrogen inside the pipe at 80 psig (0.55 MPa). The results showed that a fragment would have an initial velocity of about 79 ft/s (24 m/s), which would vertically throw it 97 feet (29.5 m). This confirmed that the roof perforations observed could have been produced by fragments from the pipe failure.

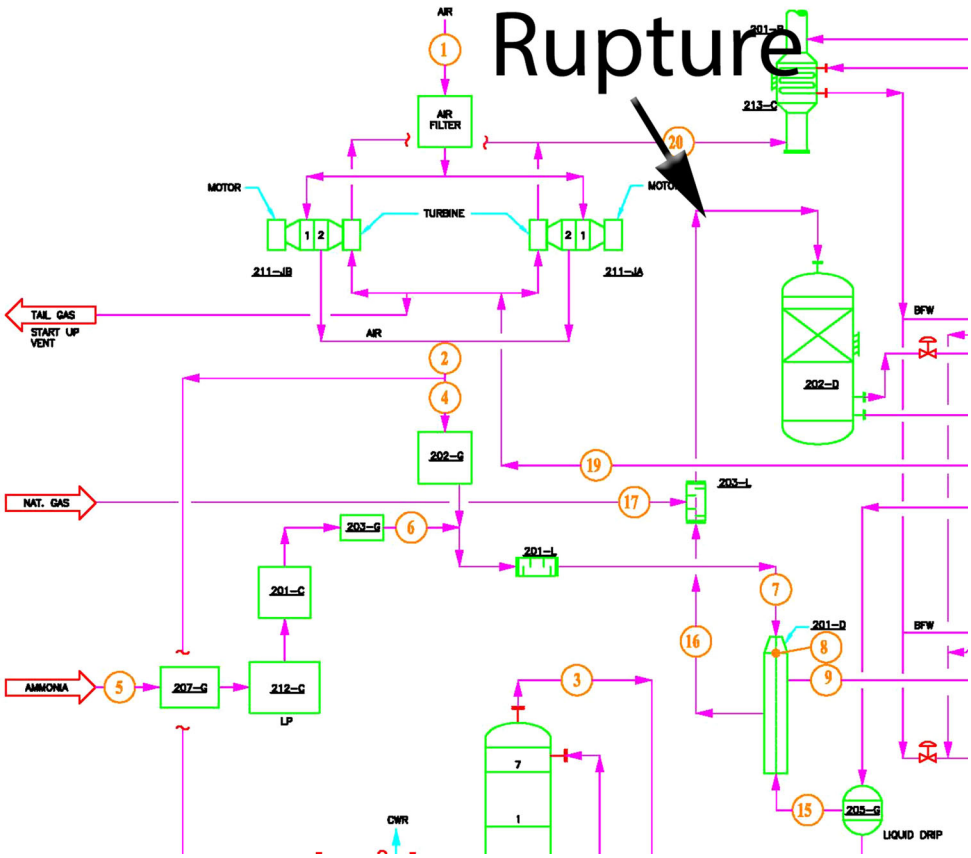

Fig. 1 Process flow diagram for the Tail Gas piping from the Converter (201-D) to the Tail Gas Catalytic Reactor (202-D)

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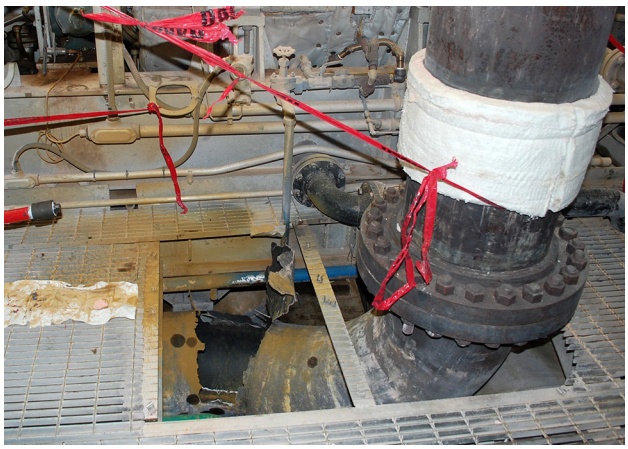

Fig. 2 Tail gas pipe failure area

Fig. 3 Failed pipe showing two wall "flaps." There was brown discoloration on the pipe, probably due to the release of NO_x

Metallurgical Analysis

Sampling

Two flap pieces at the rupture were found attached to the pipe, as shown in Fig. 9. Each flap was cut from the fractured area and labeled Piece 1 and Piece 2. These pieces are shown in Fig. 10. Piece 2, shown in Fig. 11, was primarily used for examination.

The removed section of pipe for metallurgical analysis is shown in Fig. 12. Five samples were marked for cutting from the pipe, as shown in Fig. 13, for additional analysis. The pipe section consisted of several pieces of plate formed and welded together.

The section of pipe was photographed after the five pieces were cut from the pipe as shown in Fig. 14. The cut-out rectangles were laid out in order as shown in Fig. 15.

Fig. 4 Building ceiling with fragment penetrations

Fig. 5 Broken window viewed from outside the building

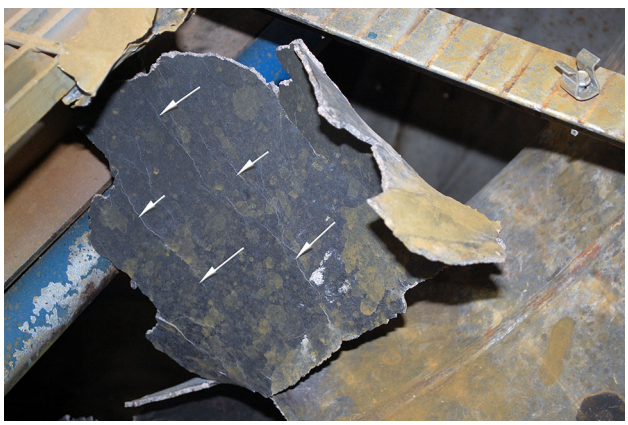

Fig. 6 Large flap showing extensive cracking on inside surface

Composition

Table 1 shows the test results for samples taken from the failed pipe. Chemical testing was performed using optical emissions spectrometry (OES). BakerRisk concluded that all samples met the standard UNS 30403 specification

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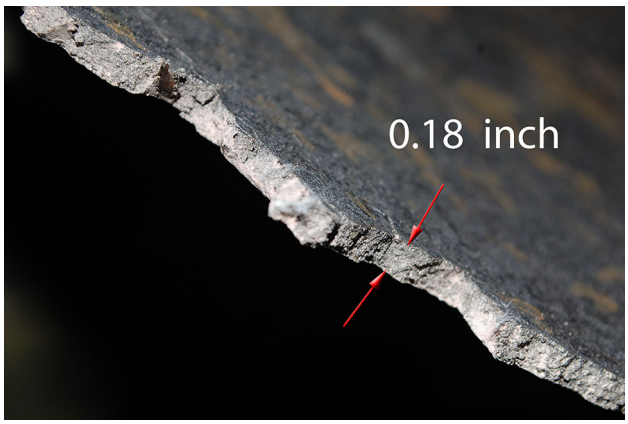

Fig. 7 Failed edge thickness similar to the nominal pipe wall thickness

Fig. 8 Stamped markings found on outer wall of Piece 2

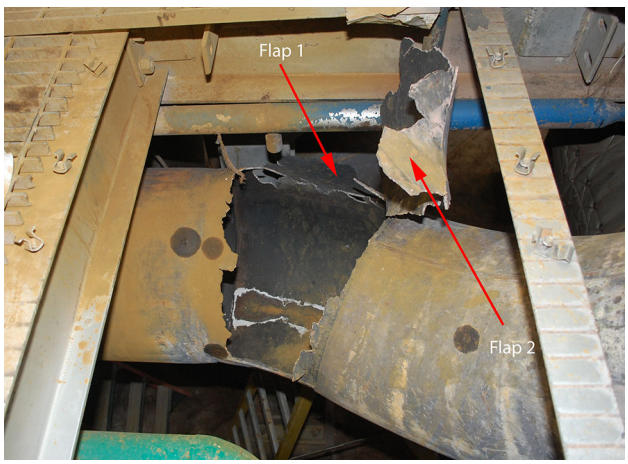

Fig. 9 View of rupture region in tail gas pipe with Flaps 1 and 2 indicated

Fig. 10 Flap Pieces 1 and 2

chemistry requirements for Type 304L stainless steel. Although not determined, the carbon weight percent may have been close to the maximum 0.03 wt.%.

Wall Thickness

Plant staff measured the pipe wall thickness at various locations upstream and downstream of the rupture region. The ultrasonic (UT)-measured wall thickness ranged from 0.172 to 0.195 in. (4.4–4.9 mm). The ruptured region wall thickness measured 0.194 in. (4.9 mm). These measurements indicated that the pipe wall did not experience a general corrosion wall thinning or ductile stretching. If the pipe was a Schedule 10, the pipe wall thickness should measure about 0.250 nominal wall thickness. Because the pipe was consistently less than 0.250-in. (6.35 mm) thick, it is likely that the original wall thickness was not Schedule 10.

Fractography

The fracture surface of Flap Piece 2 from the miter area was examined using a stereomicroscope at low magnification and the scanning electron microscope (SEM) at higher magnification. The stereomicroscope revealed a fracture that appeared to be intergranular. Using the SEM, it was determined that the predominant fracture mode was indeed intergranular, as shown in Figs. 16 and 17.

The surface of the fracture material was analyzed using energy-dispersive X-ray spectroscopy (EDS). The elements found are typical for oxides of stainless steel, with the addition of silicon and calcium.

Optical Microscopy

The fracture of Flap Piece 2 from the miter area was sectioned for metallographic examination, shown in Fig. 18.

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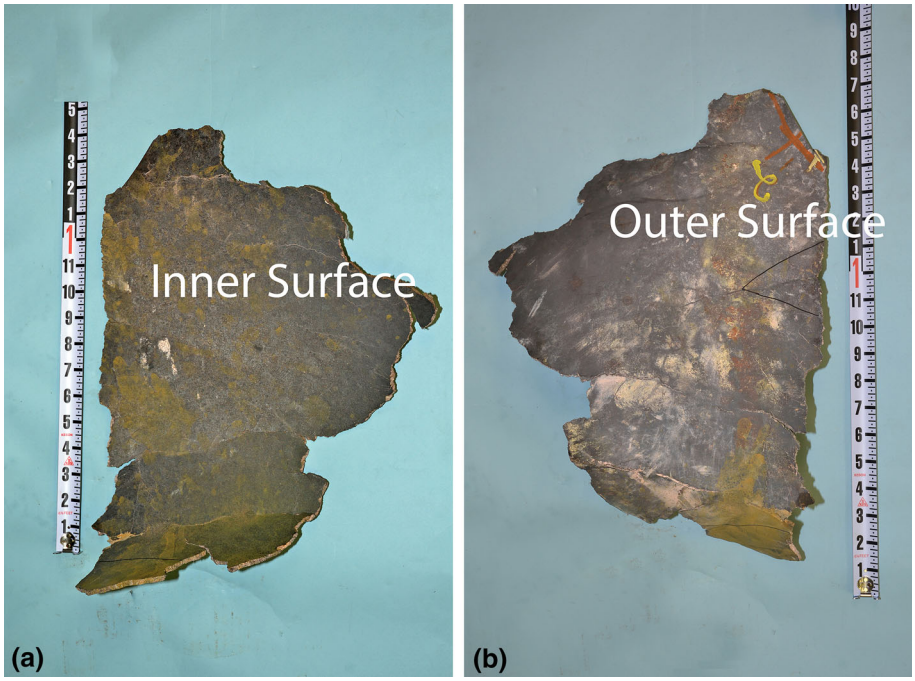

Fig. 11 Flap Piece 2 with markings for cutting at BakerRisk. Note the extensive cracking visible on the inner surface

Cracks were seen throughout this area. The cracks were intergranular, as shown in Figs. 19 and 20. The oxidized surface was analyzed by EDS and found to be typical of oxidized stainless steel as shown Fig. 21. This intergranular cracking is discussed in "Summary and Discussions" section.

Other sections of pipe outside the miter piece were examined metallographically and were found to be essentially free of cracking except for some superficial inner surface attack in the vertical pipe (one to two grains deep), as shown in Fig. 22.

ASTM A262 sensitization testing was conducted on various locations using an oxalic electrolytic etch. If the grain boundaries are "ditched" after the test, then it indicates that the material is sensitized and can have preferential corrosive attack at the grain boundaries. Figure 23 (vertical section), Fig. 24 (horizontal section), and Fig. 25 (miter section) show typical images after the specimens were exposed to the sensitization solution.

Examination of the various sections of the pipe determined the following:

- The failed miter transition region appeared to have the greatest degree of sensitization.
- The vertical elbow had some sensitization present and isolated ID surface cracks.
- The horizontal section had some sensitization with no ID surface cracking observed.

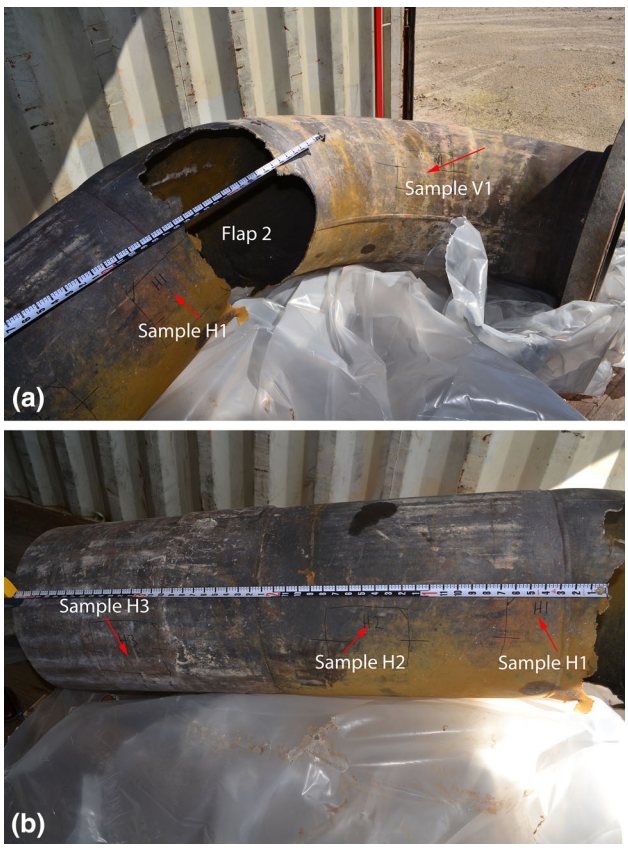

Fig. 12 Removed pipe showing locations of samples V1, H1, H2, and H3

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Hardness

The hardness of selected samples from various areas was measured directly in Rockwell B after the surface oxides were ground off. The results, shown in Table 2, were considered normal for stainless steel plate.

The hardness was measured in a transverse section through the thickness on Flap Piece 2—Mount B, using Vickers diamond pyramid microhardness at 500 g load. Figure 26 shows that the hardness was higher at the inner and outer surfaces (in the HRC range) and similar to the Rockwell B readings in the central area. The core hardness was about HV 150 (HRB 80), and the outside surface hardness was about HV 270 (HRC26). This indicates that the plate used for the miter was likely cold-worked during the rolling process at the mill and did not receive a solution annealing heat treatment after it was cold-worked. The cold-worked miter section was welded. There was also evidence of cold-working in the etched views of the microstructure.

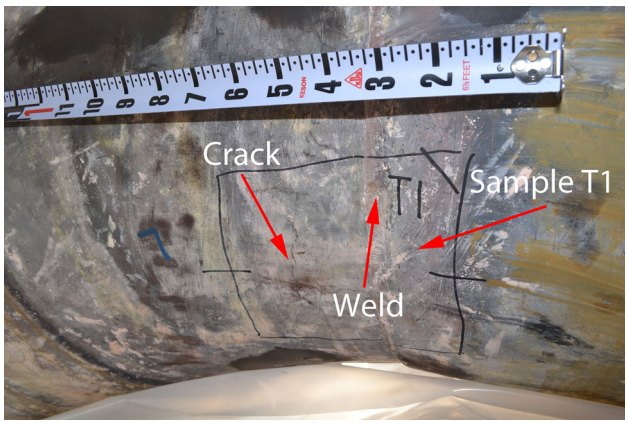

Fig. 13 Location of sample T1 marked. The weld from the miter section to the horizontal pipe is marked. Note the distance from that weld to the through-wall crack in T1 was approximately 2 in. (50.8 mm)

Fig. 14 Removed pipe showing all sample cut-out locations

Possible Scenarios

Two main scenarios were considered during the investigation: (1) that the tail gas pipe failed due to a high pressure inside the pipe from an explosion; or (2) that the pipe failed at normal operating pressure due to degradation of the pipe wall.

Failure Due to Internal Explosion

The hypothesis considered was that the pipe failed due to an internal reaction or explosion that produced a high internal pressure that failed the pipe without any degradation of the pipe itself. A simple hoop stress calculation for an 18-in. (457 mm)-diameter, 0.18-in. (0.46 mm) wall thickness stainless steel pipe gave an estimated failure pressure of about 800 psig (5.5 MPa). A stoichiometric natural gas/air mixture at an initial pressure of 80 psig (0.55 MPa) would produce a pressure of about 750 psig

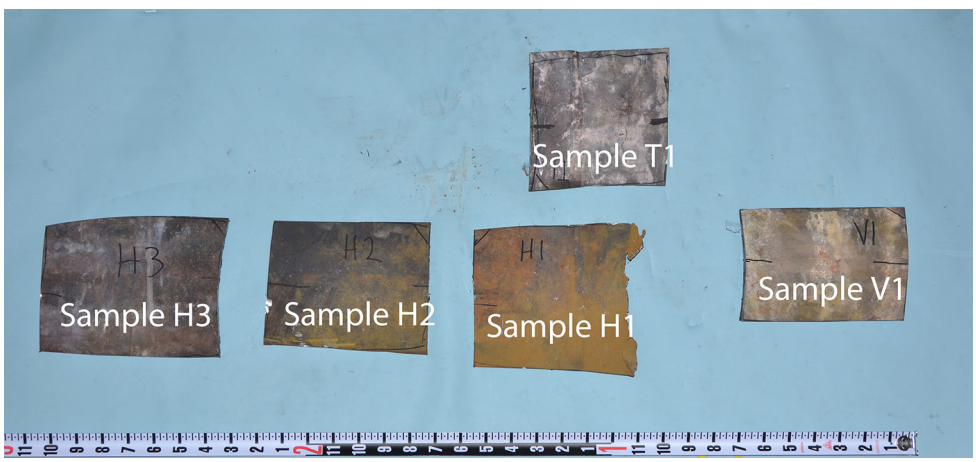

Fig. 15 Samples V1 (vertical pipe), T1 (transition pipe), H1 (horizontal pipe), H2 (horizontal pipe), and H3 (horizontal pipe) cut from pipe. The arrow points out the cracking visible on T1

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Table 1 Chemical analysis results for piping (% by weight)

Element/sample	Vertical pipe sample V1	Transition sample T1	Miter Piece 2	Horizontal pipe sample H2	Horizontal pipe sample H3	Type 304L
Carbon	0.03	0.03	0.02	0.03	0.02	0.03 Max
Manganese	1.76	1.85	1.85	1.66	1.72	2.00 Max
Silicon	0.44	0.45	0.42	0.43	0.46	1.0 Max
Phosphorus	0.031	0.035	0.031	0.030	0.030	0.045 Max
Sulfur	0.010	0.019	0.012	0.015	0.020	0.030 Max
Chromium	18.22	18.13	18.28	18.25	18.39	18.00–20.00
Nickel	8.32	8.39	8.19	8.40	8.33	8.00–12.00
Molybdenum	0.34	0.29	0.28	0.20	0.30	N/R
Copper	0.47	0.32	0.30	0.16	0.40	N/R
Iron	Balance	Balance	Balance	Balance	Balance	Balance

N/R not required

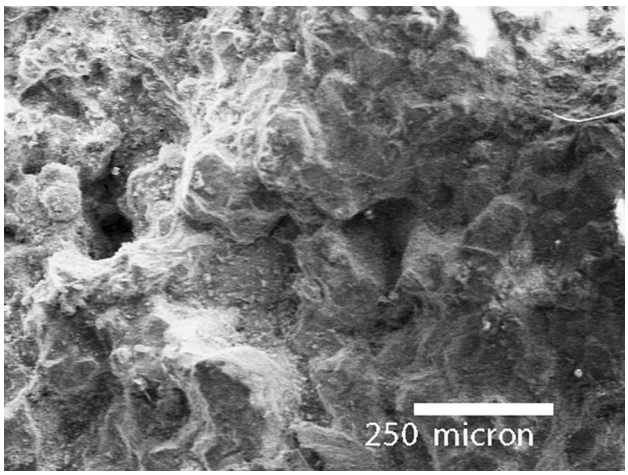

Fig. 16 SEM image of the Piece 2 fracture (before cleaning)

(5.17 MPa); therefore, the composition of the Tail Gas was examined.

From the process flow diagram, the nominal design Tail Gas flows were given both before and after the natural gas flow was added, from which the nominal concentrations were calculated. From these individual concentrations, the amount of natural gas, plus the amount of oxidizers (O_2 plus NO_x species), was found to be approximately 3% of the total gas mixture; the remainder was comprised primarily of N_2.

This dilute mixture would not support gas phase combustion and would not produce a high pressure; therefore, a flame or explosion could not have occurred in the Tail Gas piping. Even if the oxidizer or natural gas flows were off specification, the gas would remain very dilute. Only in the catalytic reactor would the oxidizers and natural gas react, as designed, to produce additional heat and reduce the NO_x concentration.

This scenario was considered to be proven false.

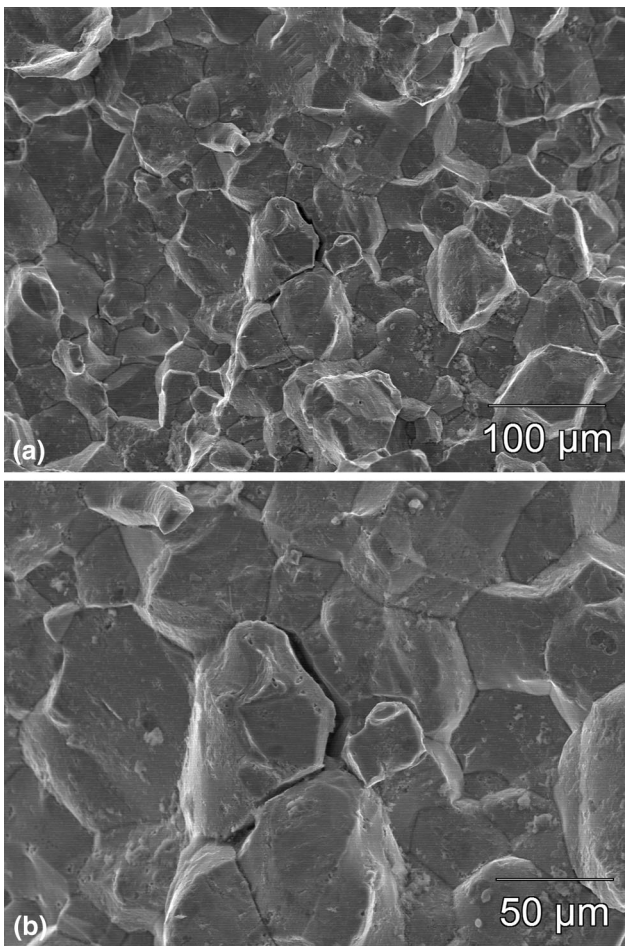

Fig. 17 SEM image of the Piece 2 fracture (after cleaning). Notice the intergranular fracture mode

Pipe Rupture: Mechanical integrity

As discussed in "Metallurgical Analysis" section of this report, the Tail Gas piping was found to be seriously

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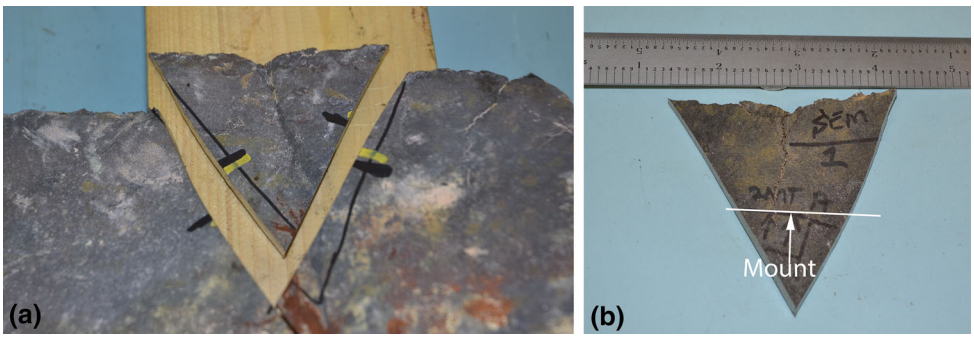

Fig. 18 Location of Piece 2—Mount A

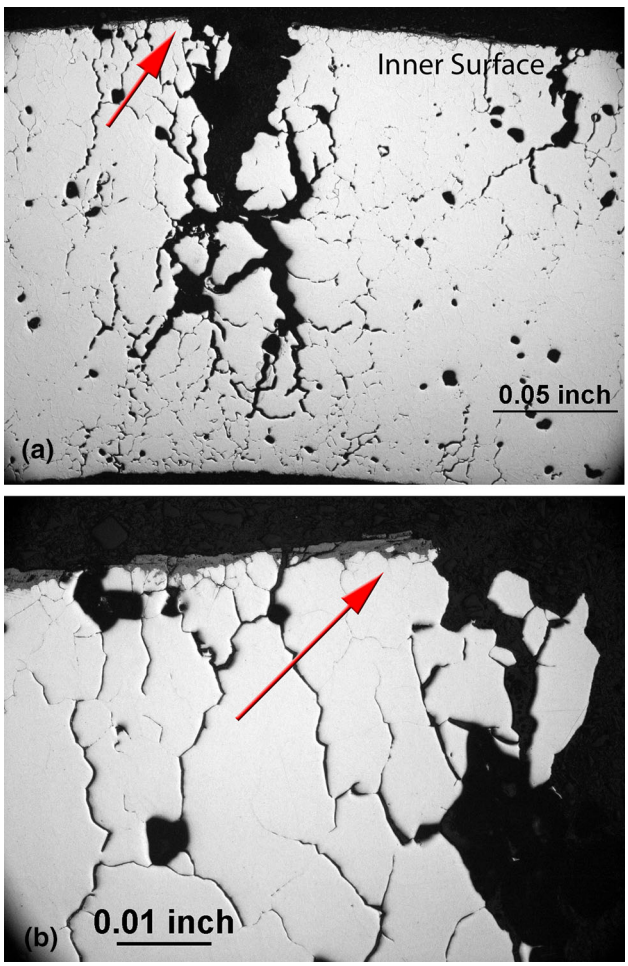

Fig. 19 Low- and intermediate-magnification view of Piece 2—Mount A (unetched)

degraded. Due to the extensive cracking, the integrity of the piping was compromised and its pressure capacity reduced. The investigation concluded that the pipe failed at the working pressure and temperature.

The metallurgical degradation of the pipe was considered the probable cause of this event.

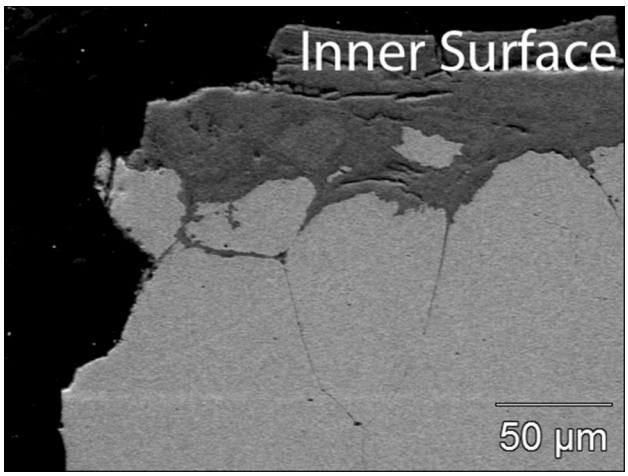

Fig. 20 High-magnification views of Piece 2—Mount A (unetched). The upper image is from the light microscope, and lower is the same area from the SEM

Summary and Discussions

The following was determined:

- The pipe ruptured at normal operating conditions due to pre-existing internal cracking of the pipe.
- There was no evidence of an internal explosion.
- A combustible mixture was not present to have caused the event. The gas mixture was predominantly nitrogen.
- The pipe was verified to be Type 304L stainless steel, which is a low-carbon austenitic stainless steel.
- The pipe failed due to intergranular stress corrosion cracking (IGSCC), as evidenced by intergranular cracks that initiated from the ID surface and extended to the outside surface. The pipe was sensitized, meaning the grain boundaries would be susceptible to attack and failure, due to long-term exposure (about 18 years) to service temperatures greater than 750 °F (400 °C).
- The acidic conditions that occurred during start-up and shutdown (when NO_x and water could condense) most likely caused an environment that caused the attack.

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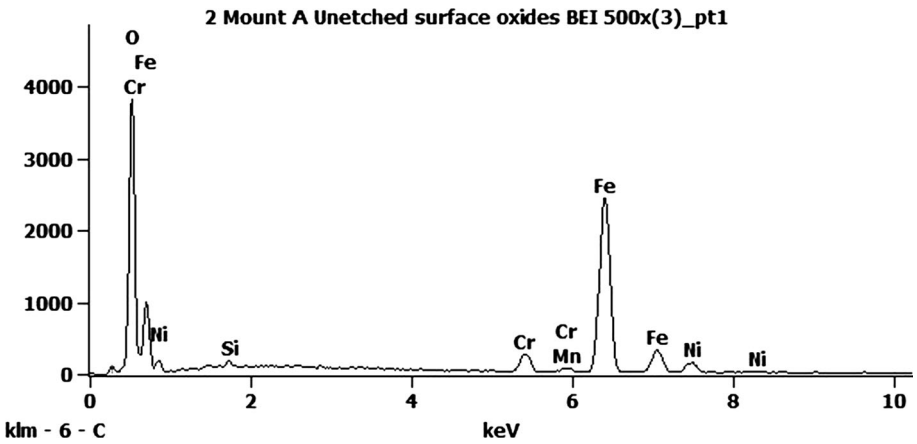

Fig. 21 Typical energy-dispersive X-ray spectrum of the surface oxides. The elements are as expected for oxides of stainless steel

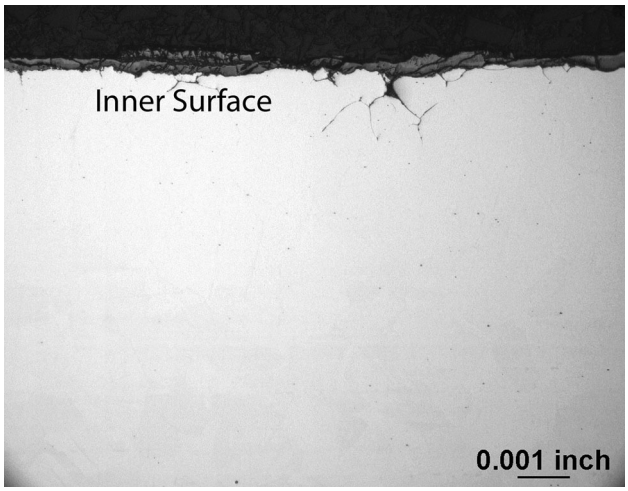

Fig. 22 Section of pipe sample V1 inner surface—Unetched. This image shows the worst attack found at the inner surface

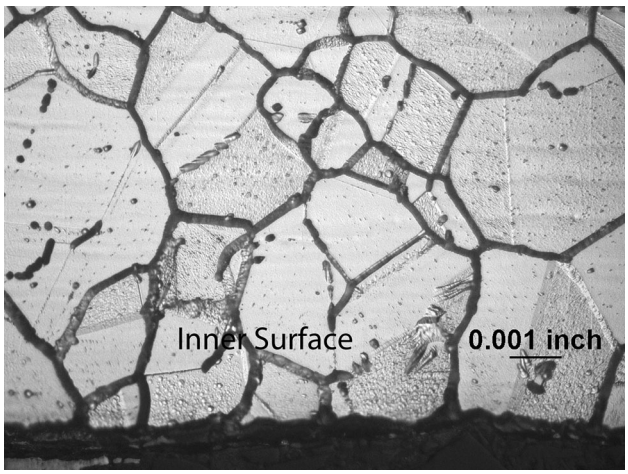

Fig. 23 Sample V1 from the vertical pipe inner surface after sensitization testing. The grain boundaries are mostly outlined by "ditching," indicating that the material was sensitized

- Other sections of the pipe also exhibited sensitization, but may not have been as highly stressed as the miter section. Those sections did not demonstrate extensive cracking.

Three factors needed for IGSSC to occur are: (1) a high tensile stress; (2) a sensitized material; and (3) an environment that can cause cracking. The pressure on the pipe was rather low, on the order of 80 psig (0.55 MPa), which would contribute to a tensile stress, but it would likely not be enough on its own to cause cracking. It is likely that other external pipe stresses existed, such as thermal fluctuations or mechanical stresses, which could have contributed to the cracking. Due to the piping configuration, the miter transition pipe likely experienced higher stresses than would the horizontal or vertical sections.

Microstructural examination and sensitization testing confirmed that the cracked miter pipe was sensitized. Sensitization occurs in austenitic stainless steels when they are exposed to manufacture, welding, and/or process

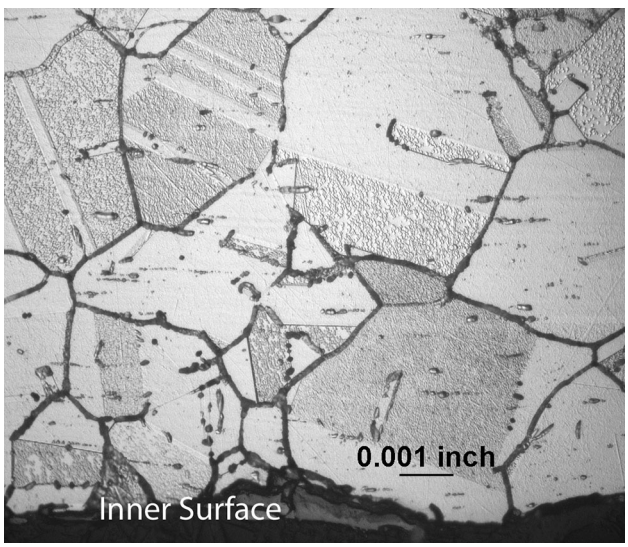

Fig. 24 Sample H3 from the horizontal pipe inner surface after sensitization testing. The grain boundaries were mostly outlined by ditching, indicating the material was sensitized

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service conditions in the temperature range of 750–1500 °F (400–815 °C). Sensitization is the formation of chromium carbides in the grain boundaries that deplete the grain boundaries of chromium, making the grains more susceptible to intergranular attack or cracking.

Type 304L, with low carbon, typically will not sensitize because of its low carbon content (<0.03 wt.%) during short welding or manufacturing exposure to high temperatures. However, Type 304L can sensitize during long-term service exposures above 750 °F (400 °C) [2].

It was shown that the miter section was cold-worked. Cold-working has also been reported to increase the susceptibility to sensitization [3]. Although Type 304L is commonly used to reduce it, sensitization can still occur at long-term exposures. Some users of Type 304L reduce the chances of sensitization by controlling the carbon content below 0.025 wt.%.

The ruptured miter transition pipe was exposed for nearly 18 years to temperatures above 750 °F (400 °C), and the pipe had evidence that suggested the plate segments were cold-worked. Both of these contributing factors would explain why the miter transition piece was sensitized and thus had a microstructure that was susceptible to IGSCC.

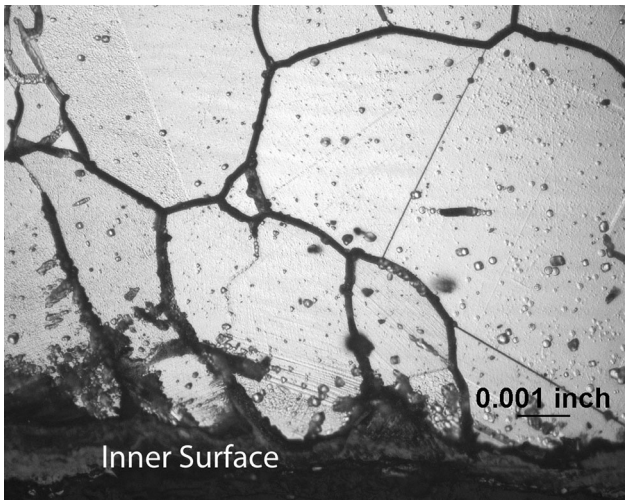

Fig. 25 Sample 2—Mount C from the miter transition section inner surface after sensitization testing. The grain boundaries were completely outlined by ditching, indicating that the material was sensitized

Because the pipe was sensitized and subject to tensile stresses, an acidic or even wet conditions could cause cracking. Because the chromium is depleted during sensitization, all that would be needed is a wet environment. During normal steady-state operations, it is unlikely that cracking would occur because the pipe contained mostly high-temperature nitrogen. The most likely times for attack would be during start-ups, down times, or a possible upset condition. The process had NO_x which could combine with moisture or condensation during downtimes and form an acidic condition that would attack the grain boundaries. During these times, the wet or acidic environment could preferentially attack the grains.

Because austenitic stainless steels (Type 316 or Type 304) or low-carbon stainless steels (Type 304L) were used for piping, other piping could be subject to the same degradation and should be inspected. Pipes in highly stressed and/or in unusual configurations may be at higher risk. Common inspection methods such as fluorescent penetrant inspection (FPI) or ultrasonic thickness (UT) wall thickness will not detect the inside surface-initiated cracking. Other inspection methods that identify internal surface-initiated cracks will need to be employed.

Mitigation Plans

As a result of the incident, several mitigation efforts were performed at the plant to address the possibility of intergranular stress corrosion cracking (IGSCC) in Type 304L

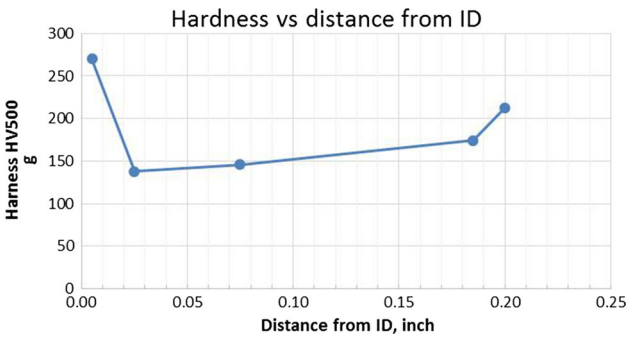

Fig. 26 Hardness vs. distance through the thickness for Piece 2—Mount B

Table 2 Hardness results for various samples, HRB

Location	Vertical pipe sample V1	Transition sample T1	Miter Piece 2	Horizontal pipe sample H2	Horizontal pipe sample H3
1	73.6	77.8	66.6	86.6	76.1
2	75.3	79.4	65.3	87.4	75.7
3	74.9	80.3	67.4	87.3	76.8
Average HRB	74.6	79.2	66.4	87.1	76.2

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in existing and new Tail Gas Systems piping exposed to temperatures greater than 750 °F (400 °C). The following items are some mitigation steps considered:

(1) *Piping Material* Instead of using Type 304L, new piping was going to be specified and replaced with Type 321 or 347 stainless steel to resist the long-term/low-temperature sensitization issue.

(2) *Pipe Inspections* Tail Gas Systems piping exposed to temperatures greater than 750 °F (400 °C) were inspected using advanced ultrasonic backscatter technique (AUBT)/phase array inspections. Exact locations for the inspections were based on an extensive process analysis looking at operating temperatures greater than 750 °F (400 °C). The analysis took into consideration all the requisites for getting into a low-temperature sensitization/intergranular stress corrosion cracking situation.

(3) *Field Fabrication Quality Control* As noted in the investigation, failure occurred in the highly stressed, field-fabricated miter section. When possible, miter joints should be pre-fabricated; however, if not possible, considerations should be given to perform subsequent solution anneal and stress relief heat treatments in the field.

(4) *Process Controls* To minimize the formation of acidic acids during downtimes and start-ups, nitrogen purge was installed to the Tail Gas line for emergency shutdown and the normal shutdown procedures were evaluated for blow through time and effectiveness: Standard operating procedures were modified accordingly to ensure all tail gas (NO_x) is removed from the piping components after emergency or normal shutdowns. This will prevent the formation of residual film nitric acid inside the pipe.

References

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